Isobaric vapor-liquid and vapor-liquid-liquid equilibrium for the system water + ethanol + n-heptane

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Heterogeneous azeotropic distillation is a widely used technique to separate binary azeotropic mixtures into their components. One of its most important applications is the dehydration of ethanol, which is blended with gasoline to obtain automobile fuel. Among all the compounds that could be used as an entrainer, heptane was chosen because it is one of the common components of gasoline. The advantage of this entrainer is that the remaining quantity of heptane in the ethanol will not be a problem for its subsequent use as a fuel. Obviously, to carry out that research, knowledge of the vapor-liquid (VLE) and the isobaric vapor-liquid-liquid equilibrium (VLLE) data is required. In this study, VLE and VLLE were measured for the ternary system water + ethanol + n-heptane at 101.3 kPa. The experimental data were correlated using NRTL and UNIQUAC and predicted with UNIFAC.

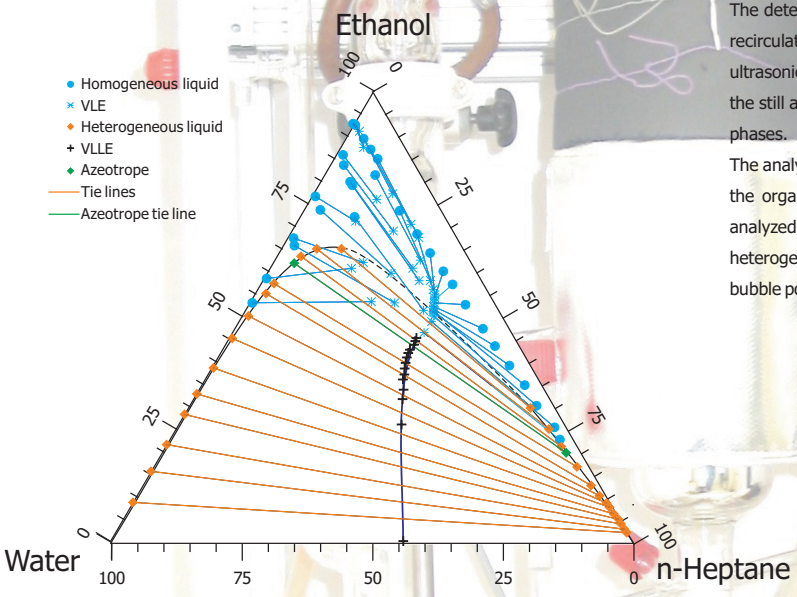

Figure 2. Experimental VLE and VLLE data at 101.3 kPa.

Figure 2 shows the experimental data obtained. They demonstrate the existence of a ternary heterogeneous azeotrope at 68.68 ºC. The mole fractions of the components of this experimental azeotrope are 0.206, 0.432, and 0.363, for water, ethanol and n-heptane, respectively. These results are similar to those previously obtained by Fritzweiler and Dietrich (0.363, 0.403, 0.334 at 68.00ºC). Consequently, heptane could be used as an entrainer for the ethanol dehydration.

The determination of vapor-liquid-liquid equilibrium data was carried out in an all-glass dynamic recirculation still with an ultrasonic homogenizer coupled to the boiling flask (figure 1). The use of ultrasonic sound on the boiling flask causes the emulsification of the two liquid phases throughout the still and thus prevents the oscillations in temperature and flow rate of systems with two liquid phases.

The analysis of the equilibrium phases was carried out by gas chromatography, except for water in the organic phase, which was determined by the Karl Fischer method. The vapor phase was analyzed without prior condensation to prevent phase split. For the sampling of the liquid phases, a heterogeneous dispersed sample was placed in a tube where it splits into two liquid layers at their bubble point. Samples of each layer were taken later to be analyzed.

Figure 1. Experimental equipment.

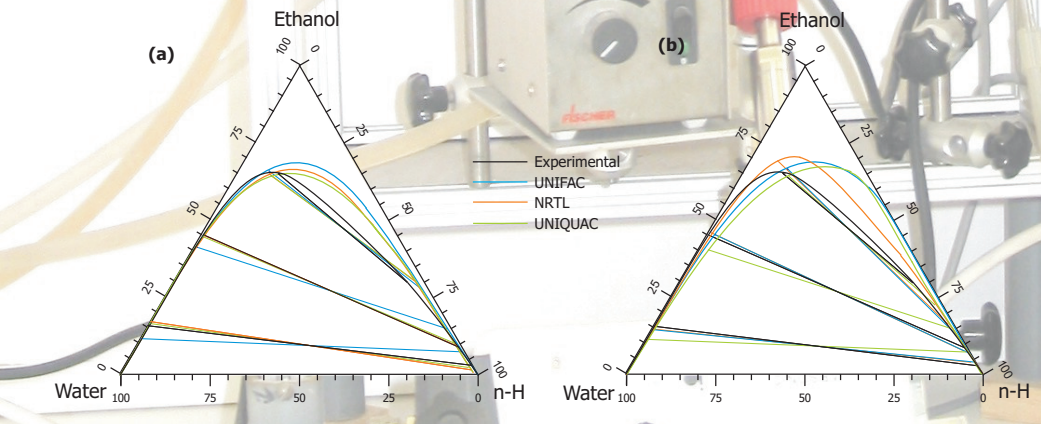

Figure 3. Experimental and calculated LLE data.

Figure 3 shows the graphical representation of three different experimental tie lines compared with those obtained using UNIQUAC and NRTL by correlation of either only the LLE data (figure 3a) or the VLE and VLLE data simultaneously (figure 3b). Results with LLE UNIFAC (figure 3a) and original UNIFAC (figure 3b) are also shown. None of these methods properly correlate and approximate the top zone of the non isothermal solubility curve, which is important to the simulation of the azeotropic distillation.